

530,682

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property  
Organization  
International Bureau



(43) International Publication Date  
22 April 2004 (22.04.2004)

PCT

(10) International Publication Number  
**WO 2004/033545 A1**

- (51) International Patent Classification<sup>7</sup>: **C08K 5/00 //** (C08K 5/00, 5:13, 5:527, 5:372)
- (21) International Application Number: PCT/EP2002/011258
- (22) International Filing Date: 8 October 2002 (08.10.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (71) Applicant (for all designated States except US): **BOREALIS TECHNOLOGY OY** [FI/FI]; P.O. Box 330, FIN-06101 Porvoo (FI).
- (72) Inventors; and
- (75) Inventors/Applicants (for US only): **ØYSÆD, Harry** [NO/NO]; Brattelia 1C, N-3960 Stathelle (NO). **JAMTVEDT, Svein** [NO/NO]; Blåbærv. 1, N-3960 Stathelle (NO). **FRØHAUG, Astrid, E.** [NO/NO]; Pekestokken 7, N-3960 Stathelle (NO).
- (74) Agent: **NOBBE, Matthias**; Viering, Jentschura & Partner, Centroallee 263, 46047 Oberhausen (DE).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- Published:**  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: STABILIZED POLYMER COMPOSITION

(57) Abstract: The present invention relates to an antioxidant composition comprising (a) 0.01-0.5% by weight of sterically hindered phenolic compound, (b) 0.01-0.5% by weight of phosphorous compound, and (c) 0.01-1% by weight of sulphurcontaining compound. Said antioxidant composition reduces degradation of plastic materials during processing and end-use and thus, increases the long term thermal stability of those plastic materials. Moreover, this invention relates to methods for producing a final polymeric article with an increased long term thermal stability and stabilization against ageing by radical decomposition processes and polymeric intermediate materials as well as polymeric articles comprising the inventive antioxidant composition.



WO 2004/033545 A1

REC'D 07 APR 2005

Stabilized polymer compositionTechnical field

5 The present invention relates to a stabilized polymer  
composition comprising a composition of antioxidants which  
reduces degradation of plastic materials during processing  
and end-use and thus, increases the long term thermal  
stability of those plastic materials. Moreover, this  
10 invention relates to methods for producing a final polymeric  
article with an increased long term thermal stability and  
stabilization against ageing by radical decomposition  
processes and polymeric intermediate materials as well as  
polymeric articles comprising the inventive antioxidant  
15 composition.

Background art

Recent advances in the manufacturing and processing of  
20 plastic polymers have led to the application of plastics in  
virtually every aspect of modern day life. However, polymeric  
compounds are prone to ageing under the effects of light,  
oxygen and heat. This results in a loss of strength,  
stiffness and flexibility, discolouration and scratching and  
25 loss of gloss.

Polymeric compounds, for example polyolefines like  
polyethylene and polypropylene undergo radical driven  
degradation processes especially during processing steps  
30 which might include moulding, extrusion etc. However,  
degradation even proceeds during end-use by a radical  
mechanism under the influence of light, heat etc. and will  
finally destroy the polymer properties.

It is well-known in the art that antioxidants and light stabilizers can prevent or at least reduce these effects. Several types of additives are added to polymers to protect them during processing and to achieve the desired end-use properties. Additives are generally divided in stabilizers and modifiers. Typical modifiers are antistatic- and anti-fogging agents, acid scavengers, blowing agents, cling agents, lubricants and resins, nucleating agents, slip- and anti-blocking agents as well as fillers, flame retardants, compatibilizers and crosslinkers.

Antioxidants traditionally and currently used comprise hindered phenolics, aromatic amines, organo-phosphites/phosphonites and thioethers. Neutralizers are often used to boost performance and diminish effects of residual polymer acidity.

Because of its sensitivity to oxidation, stabilization of polypropylene polymers against thermal oxidation is extremely important. Polypropylene polymers are probably the polymer most studied in this respect. At elevated temperatures and with excess of air, polypropylene polymers disintegrate to powdery oxidation products. This process is characterized by relatively well-defined and reproducible induction periods, commonly called oven lifetimes. Endpoints are easily detected even visually. The disintegration begins mostly at the etches and corners of the test species. It is often accompanied by yellow to brown discoloration.

An important aspect of process stabilization is that the degradation reaction products produced during processing can accelerate other types of a degradation later in the polymer life time, e.g. impede the light stability of the polymer.

For this reason, effective processing stability is essential in the production of durable plastic and articles.

Long term heat stability (LTHS) is an important property for many applications of polymers, especially polyolefines. Generally, long term thermal stability requirements are met by adding high concentrations of phenol antioxidants or combinations of phenols and thioethers to the polymer. Problems with such systems may be that tendency to yellowing increased by increased phenol concentrations or that the thioether may influence organoleptic properties in a negative way.

There are several approaches known in the prior art which address the problem of stabilization of polymers against radical decomposition which among others finally results in a loss of long term thermal stability of a polymer.

For example, US 6,015,854 teaches propylene-ethylene copolymers of high clarity and therefore incorporates clarifying agents into the copolymer mixture, however, the compositions disclosed therein may also contain stabilizers, antioxidants, lubricants, acid acceptors, synergists, anti-static agents, nucleating agents and additives which stabilize against radiation. To improve long term thermal stability, primary antioxidants of phenolic-type were added. Furthermore, it is stated that second type antioxidants like phosphites or hindered amines provide for an improved stability in melt flow and colour during the melt processing of the plastic material. The functions of all other primary and secondary antioxidants mentioned in the reference are well-known in the art. It is also disclosed that the synergistic enhance of the primary antioxidants can be achieved by including thioethers. However, this reference

focuses on clarity of the plastic material and consequently none of the properties measured in the examples is related to long term heat stability.

5 US 6,022,946 is directed to a method of deactivating catalyst residue in a polyolefin in a post-reactor vessel containing carbon monoxide. Claim 1 mentions the incorporation of an acid acceptor and at least one secondary antioxidant into the deactivated polyolefin polymer. This secondary antioxidant  
10 may be an organic phosphite. Primary antioxidants including phenolic types are also mentioned with the main function to provide long term thermal stability. The synergistic enhance of this performance by including thioethers is also noted. Secondary antioxidants including phosphites are mentioned  
15 which provide for improved colour and reduced melt flow breaking tendency. Again, this reference does not teach anything going beyond the general knowledge in the art according to which long term thermal stability can be controlled by the addition of a primary antioxidant and  
20 optionally a synergistic thio-compound.

Though US 6,197,886 relates to polypropylene impact copolymers having improved mechanical properties, similar comments can be provided again.. There are polymeric  
25 compositions disclosed which may contain antioxidants. Primary antioxidants, including phenolic types are mentioned with the main function to provide long term heat stability. The synergistic enhance of this performance by including thioethers is also mentioned. Furthermore, addition of  
30 secondary antioxidants including phosphites with the focus on the improvement of the melt processing are disclosed as well. However, nothing can be taken from that reference which would enable the skilled artisan to achieve an improved long term thermal stability exceeding those already known in the art.

Furthermore, US 6,090,877 relates to a low smoke forming, acid neutralized propylene polymer composition comprising a propylene and an acid scavenging amount of mono potassium citrate. Phenolics and phosphites are mentioned as possible antioxidants for polypropylene together with potassium citrate as an acid scavenger but this reference is quiet with regard to long term thermal stability of the propylene polymer compositions.

10

Another prior art reference (Zweifel, H., Stabilization of Polymeric Materials, Springer-Verlag, 1998, p. 76) reflects the general and well-established view in the art on the best mode to control long term thermal stability in polymers:

15

"In contrast to stabilization during processing, the presence of phosphites had not significant influence on long term thermal ageing of polyolefines".

20 Likewise, Schwartzenbach et al., in Zweifel's, Plastic Additives Handbook, 5th edition, Hanser Publishers, 2001, p. 53 states:

25 "Phosphites do not contribute to long term thermal stability themselves. Long term thermal stability is only protected by the available phenol concentration. To improve long term thermal stability, thiosynergists as hydroperoxide decomposers in combination with a phenol are recommended."

30 Though, the necessary level of long term stability of a specific plastic material very much depends on the intended technical application thereof, there still exists a continued need for an improved control of this polymer property during processing steps and end use of the polymer. As discussed

above, the prior art teaching suggests to apply an antioxidant composition of a phenolic compound and a thiosynergist for hydroperoxide decomposition to the polymeric base material to reduce long term thermal ageing.

5

Therefore, the major focus to increase long term thermal stability of a polymer relied so far in the provision of improved phenolic-type and thioether antioxidants. That is to say, specific antioxidant compounds were developed which provide for example for a low volatility, high melting point, hydrolytic and thermal stability as well as the absence of unwanted side effects like having a colouring effect or an unclean toxicological profile which could jeopardize FDA and/or EU-SCF approvals. Most of those properties of the state of the art antioxidants are met by the unique structural features of these compounds, for example bulky residues of tert.-butyl substituted phenyl residues which provide for sterical hindrance to lower volatility in combination with a high molecular weight of those compounds.

20

In the state of art, the most obvious way to further increase long term thermal stability is generally seen in the use of higher amounts of those antioxidants. However, it is likewise obvious that simply increasing the antioxidant concentration in the polymer composition will most likely affect the properties of the final plastic material in a negative way. Therefore, it is highly desirable to be able to reduce long term thermal ageing with even less antioxidant compounds used in the polymer composition.

25  
30

#### Description of the invention

The inventors of the present application have addressed this issue by a different approach than those described above in

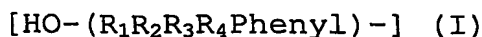
the prior art. The underlying problem of this invention is to be seen in the provision of polymers comprising specific antioxidant compositions which already allow to improve long term thermal stability of said polymeric material at very low concentrations of antioxidant compounds. Moreover, at the same time this stability towards thermal ageing should be further increased in view of long term thermal stabilities achieved so far by prior art approaches. Furthermore, such a composition of antioxidants should provide for a highly effective and versatile stabilization which is useful in a wide variety of applications. Likewise, this composition should be characterized by its superior thermal stability and low volatility, excellent atmospheric and in-polymer hydrolytic stability, outstanding protection against discoloration and degradation during processing, and excellent protection against long term polymer degradation.

In accordance with this objective, and other objectives that will be readily apparent to those skilled in the art upon reading this disclosure, it was surprisingly found that the specific combination of a phenolic compound together with a phosphite and a sulphur-containing compound substantially increase the long term heat stability of a polymer at unexpected low concentrations.

In accordance with the invention, it is provided a stabilized polymer composition comprising a polymer and an antioxidant composition for improving the long term heat stability of polymers, in particular polyolefins, said polymer composition comprising:

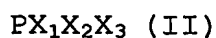
(a) 0,01% - 0,5% by weight of at least one sterically hindered phenolic compound, wherein said phenolic compound contains at least one phenolic moiety of general formula (I):





wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  or  $\text{R}_4$  may be the same or different and at least one of  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  or  $\text{R}_4$  is selected from the group consisting of branched alkyl having 1 to 12 carbon atoms, preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl, the others of  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  or  $\text{R}_4$  being H or lower alkyl having 1 to 6 carbon atoms;

(b) 0,01% - 0,5% by weight of at least one phosphorous compound, wherein said phosphorous compound contains at least one phosphorous compound moiety of general formula (II):



wherein  $\text{X}_1$  may be  $\text{R}_5$  or  $\text{OR}_5$ ,  $\text{X}_2$  may be  $\text{R}_6$  or  $\text{OR}_6$ ,  $\text{X}_3$  may be  $\text{R}_7$  or  $\text{OR}_7$  and  $\text{R}_5$ ,  $\text{R}_6$  or  $\text{R}_7$  may be the same or different and at least one of  $\text{R}_5$ ,  $\text{R}_6$  or  $\text{R}_7$  is selected from the group consisting of  $\text{C}_1$ - $\text{C}_{25}$  alkyl group, aryl group or aralkyl group which may be substituted by lower alkyl having 1 to 6 carbon atoms, or two or any of  $\text{R}_5$ ,  $\text{R}_6$  or  $\text{R}_7$  may form a ring structure having 4 to 12 carbon atoms,

(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):



wherein  $x = 1$  or  $2$ , and wherein  $\text{R}_8$  and  $\text{R}_9$  may be the same or different and are selected from the group consisting of  $\text{C}_{10}$ - $\text{C}_{25}$  alkyl groups optionally being substituted with  $\text{C}_1$ - $\text{C}_{12}$  alkyl ester carboxylates, wherein said % by weight values are referred to the polymer composition.

In a preferred embodiment, the stabilized polymer composition comprises a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

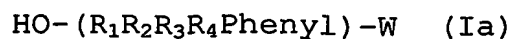
- 5 (a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,  
(b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and  
(c) 0,05% - 0,6% by weight of said at least one sulphur-  
10 containing compound of general formula (III),  
wherein said % by weight values are referred to the polymer composition.

In a further preferred embodiment, the stabilized polymer  
15 composition comprises a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

- (a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,  
(b) 0,05% - 0,15% by weight of said at least one  
20 phosphorous compound, and  
(c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III),  
wherein said % by weight values are referred to the polymer composition.

25 When using the inventive antioxidant composition, further compounds selected from additives, fillers, minerals and lubricants can be compounded to the polyolefin for improving the processability and surface characteristics thereof.

30 The phenolic compound contains preferably at least one phenolic moiety of general formula (Ia):



wherein  $R_1$  and  $R_4$  being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched  $C_1$  to  $C_{12}$  alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues,  $R_2$  and  $R_3$  having the meaning as given before, and W is selected from  $C_1$  to  $C_{12}$  alkyl,  $C_1$  to  $C_{12}$  alkoxy,  $C_1$  to  $C_{12}$  alkyl carboxylate or  $C_1$  to  $C_{12}$  alkyl substituted by a further group of the formula HO-  
( $R_1R_2R_3R_4$ Phenyl)-, wherein  $R_1$  to  $R_4$  have the meaning as indicated before.

In accordance with the present invention, it is particularly preferred that at least one of the following phenolic-type antioxidant compounds is comprised by the inventive antioxidant compositions. These are the sterically hindered phenolic compounds:

- 2,6-Di-tert.-butyl-4-methyl phenol;
- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethyl-phosphonate);
- 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester;
- 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);
- 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);

- N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxy-hydrocinnamamide;
- 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl) chroman-6-ol;
- 5 - 2,2'-Ethylidenebis (4,6-di-tert.-butylphenol);
- 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-butylphenyl) butane;
- 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl) -1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;
- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro
- 10 (5,5)undecane;
- 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);
- 2,6-Di-tert.-butyl-4-nonylphenol;
- 15 - 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris (2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione;
- 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);
- 2,2'-Methylene bis (4-methyl-6-tert.-butylphenol);
- 20 - 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl)propane;
- Triethyleneglycole-bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl) propionate;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C<sub>13</sub>-C<sub>15</sub>-branched and linear alkyl esters;
- 25 - 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
- Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl)phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- 30 - Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C<sub>7</sub>-C<sub>9</sub>-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and

- a butylated reaction product of p-cresol and dicyclopentadiene.

Among those compounds, the following phenolic-type

5 antioxidant compounds are especially preferred to be included in the antioxidant composition according to the present invention:

- Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- 10 - Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-
- 15 isocyanurate.
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester; and
- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro
- 20 (5,5)undecane;

Furthermore, it is preferred that the phosphorous compound of the inventive antioxidant compositions contains a phosphite moiety of general formula bis(R<sub>10</sub>)-pentaerythritol-

25 diphosphite, wherein R<sub>10</sub> is selected from C<sub>1</sub>-C<sub>25</sub> alkyl group or aryl group which may be substituted by lower alkyl having 1 to 6 carbon atoms.

In accordance with the present invention, it is also

30 preferred that at least one of the following phosphorous-type antioxidant compounds is comprised by the inventive antioxidant compositions. These are the phosphorous compounds:

- Tris (2,4-di-t-butylphenyl) phosphite;

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite
- Bis (2,4-di-t-butylphenyl)-pentaerythrityl-di-phosphite;
- Di-stearyl-pentaerythrityl-di-phosphite;
- 5 - Tris-nonylphenyl phosphite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 2,2'-Methylenebis (4,6-di-t-butylphenyl) octyl-phosphite;
- 1,1,3-Tris (2-methyl-4-ditridecyl phosphite-5-t-
- 10 butylphenyl) butane;
- 4,4'-Butylidenebis (3-methyl-6-t-butylphenyl-di-tridecyl) phosphite;
- Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;
- Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous
- 15 acid ethylester;
- 2,2',2''-Nitrilo triethyl-tris(3,3',5,5'-tetra-t-butyl-1,1'-biphenyl-2,2'-diyl)phosphite);
- Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester;
- 20 - Bis (2,4,6-tri-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 2,2'-Ethylidenebis (4,6-di-t-butylphenyl) fluorophosphonite
- 6- (3-tert-Butyl-4-hydroxy-5-methylphenyl) propoxy)-2,4,8,10-tetra-tert. butyldibenz (d,t)(1.3.2) dioxaphosphopin; and
- 25 - Tetrakis-(2,4-di-t-butyl-5-methyl-phenyl)-4,4'-biphenylen-di-phosphonite

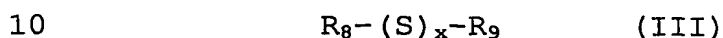
Among those compounds, the following phosphite/phosphonite-type antioxidant compounds are especially preferred to be

30 included in an antioxidant composition according to the present invention:

- -

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 5 - Di-stearyl-pentaerythrityl-di-phosphite; and
- Bis(2,4-dicumylphenyl)pentaerythritol diphosphite.

In accordance with the present invention, the sulphur-containing compound of general formula (III):



is selected from Di(C<sub>1</sub>-C<sub>20</sub>)alkyl-(S)<sub>x</sub>-di-carboxylate wherein the carboxylic acid is selected from C<sub>1</sub> to C<sub>10</sub> alkyl carboxylic acids. Some of those preferred compounds are exemplified as follows:

- 15 - Di-stearyl-thio-di-propionate;
- Di-palmityl/stearyl-thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- Di-myristyl-thio-di-propionate;
- 20 - Pentaerythritol octyl thiodipropionate;
- Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide; and
- Pentaerythritol-tetrakis-(3-laurylthiopropionate);
- 25 wherein Di-stearyl-thio-di-propionate and Di-tert-dodecyl-disulphide are especially preferred.

In a particularly preferred embodiment, the inventive antioxidant composition is such that it comprises a mixture

30 of, as the sterically hindered phenolic compound, 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-Butyl-4-hydroxyphenyl)-propionate,

as the phosphite compound, bis(2,4-dicumylphenyl)pentaerythritol diphosphite; and, as the sulphur-containing compound, di-stearyl-thio-di-propionate. Moreover, the inventive antioxidant composition may optionally further comprise metal deactivators and/or UV-stabilisers, wherein preferably said UV-stabilizers are sterically hindered amines.

It is another object of the present invention to provide a polymeric material which comprises the above-described antioxidant composition and at least one polymer selected from the group consisting of polyolefines, polyethers, polyimides, polyamides and polyesters. If said at least one polymer comprises a polyolefin, it is preferred that the polyolefin polymer is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

In accordance with a further object, the present invention, provided for the use of the above-described antioxidant composition to reduce degradation of a polymeric material by radical mechanisms during processing and end use of said polymeric material and preferably to increase the long term thermal stability of the polymeric material.

In yet another object of the present invention, there is provided a method for producing a final polymeric article with an increased long term thermal stability against ageing by radical degradation processes comprising the steps of:

- (a) providing an unstabilised base polymer material;
- (b) adding to said base polymer material the inventive antioxidant composition;
- (c) converting the composition obtained in step (b) in a melt-forming process; and



(d) confectioning the polymeric material obtained in step (c).

This method may optionally include the further step

5 concerning the addition of other stabilisers and/or modifiers before the converting step.

The converting step typically includes injection moulding, blow moulding, rotational moulding and/or extrusion and the  
10 confectioning step generally comprises cutting, lamination and/or welding.

Furthermore, it is still another object of the present invention to provide a polymeric article having a long term  
15 ageing stability and being obtainable by one of the above-described methods for producing a final polymeric article.

#### Examples

In each of the following formulations of antioxidant  
20 compositions, the thioether Di-stearyl-thio-di-propionate was used as the sulphur-containing compound (c) at a concentration of 3000 ppm. Furthermore, a polypropylene homopolymer in form of an unstabilised powder was selected to verify the effect of the inventive antioxidant compositions  
25 on long term thermal stabilization. Beside the inventive antioxidant compositions, only 600 ppm Ca-stearate and partly 2000 ppm talc were further included into the polymer mixture as non-antioxidant additives where indicated.

30 The compounding steps were carried out for each formulation in a Prism extruder at the extruder condition of 210°C, 1 bar N<sub>2</sub>.

Base polymer:

PP-homopolymer unstabilised powder mfr (230°C/2.16 kg) 3 g/10 min.

Non-antioxidant additives:

- 5 Ca-stearate (Calcium stearate SP, Faci, NO1,), talc (Tital 10, Incemin AG, NO2,)

Antioxidant additives:

(a) Phenolic-type compound (I)

- 10 - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate (Irganox 1010 <sup>TM</sup>, Ciba Specialty Chemicals, AO-I-1),  
- 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (Cyanox 1790 <sup>TM</sup>,  
15 Cytec, Inc., AO-I-2),

(b) Phosphite-type compound (II)

- Tris(2,4-di-t-butylphenyl)phosphite (Irgafos 168 <sup>TM</sup>, Ciba Specialty Chemicals, AO-II-1),  
20 - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite (Doverphos S-9228 <sup>TM</sup>, Dover Chemical Corp., AO-II-2)

(c) Sulphur-containing compound (III)

- Di stearyl-thio-di-propionate (Irganox PS-802, Ciba  
25 Specialty Chemicals, AO-III)

Table 1 provides an overview of the concentration of each antioxidant and non-antioxidant additive which are incorporated into the polypropylene homopolymer compositions  
30 of Examples 1-10.

After prism extrusion, MFR and YI were determined for each sample. With regard to Examples of Ref. No. 1,3 and 7-10 multiple extrusion at a Brabender extruder were carried out.

Long term heat stability was determined for each sample on pellets at 150°C. When degraded pellets were observed for the first time the YI value was then measured.

- 5 All results of these determinations are summarized in Table 2.

Table 1

Ref. No.	Antioxidant additives						Non-antioxidant additives	
	Phenolic type AO			Phosphite-type AO		Sulphur- containing AO		
	AO-I-1	AO-I-2	AO-I-3	AO-II-1	AO-II-2			
1	1200 ppm	-	-	2400 ppm	-	3000 ppm	600 ppm	2000 ppm
2	1200 ppm	-	-	-	1600 ppm	3000 ppm	600 ppm	2000 ppm
3	1200 ppm	-	-	-	800 ppm	3000 ppm	600 ppm	2000 ppm
4	-	600 ppm	-	1600 ppm	-	3000 ppm	600 ppm	2000 ppm
5	-	300 ppm	-	1600 ppm	-	3000 ppm	600 ppm	2000 ppm
6	-	600 ppm	-	-	800 ppm	3000 ppm	600 ppm	2000 ppm
7	-	300 ppm	-	-	800 ppm	3000 ppm	600 ppm	2000 ppm
8	1200 ppm	-	-	2400 ppm	-	3000 ppm	600 ppm	-
9	1200 ppm	-	-	-	800 ppm	3000 ppm	600 ppm	-
10	-	300 ppm	-	-	800 ppm	3000 ppm	600 ppm	-

Table 2

Ref. No.	mfr after multiple extrusion					YI after multiple extrusion					long term heat stability	
	0.	1.	3.	5.		0.	1.	3.	5.		hours to degrad.	YI after degrad.
1	3,1	3,3	3,7	3,8		-1,4	-1,6	0	1,3		2620	43
2	3,0	-	-	-		-1,5	-	-	-		3070	46
3	3,0	3,2	3,5	3,7		-1,6	-1,1	1,7	3,4		3020	47
4	2,9	-	-	-		-0,8	-	-	-		2500	47
5	3,0	-	-	-		-1,7	-	-	-		2280	35
6	3,0	-	-	-		-1,0	-	-	-		3070	47
7	3,0	3,2	3,6	3,9		-1,7	-0,9	1,7	3		3020	36
8	3,0	3,2	3,6	3,7		-1,9	-1,6	-1,1	0,4		2620	42
9	3,0	3,2	3,5	3,9		-2,2	-2,0	-0,8	0,3		3020	47
10	3,0	3,2	3,8	4,3		-2,4	-1,6	-0,6	0,2		3120	38

Effect of Bis(2,4-dicumylphenyl)pentaerythritol diphosphite on process stability and LTHS

The equal mfr values after compounding (3,0 +/-0,1) for all of the formulations show a very good process stabilising in each sample.

In the series of Ref. No. 1-3, Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate (Irganox 1010 <sup>TM</sup>, AO-I-1) is constant, and 2400 ppm Tris(2,4-di-tert-butylphenyl)phosphite (Irgafos 168 <sup>TM</sup>, AO-II-1) is compared with 1600 ppm and 800 ppm of Bis(2,4-dicumylphenyl)-pentaerythritol diphosphite (Doverphos S-9228 <sup>TM</sup>) (AO-II-2). The results of mfr and YI after multiple extrusions are similar, though a little stronger yellowing effect was observed after the 5th extrusion of the sample comprising 800 ppm Doverphos S-9228 <sup>TM</sup> (AO-II-2).

Figure 1 shows a comparison of LTHS values (hours at 150°C before start of degradation) for the formulations with 1200 ppm Irganox 1010 <sup>TM</sup> (AO-I-1). It can be taken from these results that, in contrast to the generally acknowledged opinion in the prior art, the phosphite also influences LTHS. An increase of more than 400 hours at 150° by replacing 2400 ppm Irgafos 168 <sup>TM</sup> (AO-II-1) with 800 ppm Doverphos S-9228 <sup>TM</sup> (AO-II-2) is quite considerable. Doubling the amount of Doverphos S-9228 <sup>TM</sup> (AO-II-2) only gives a slight increase in LTHS. This proves that a smaller amount of the preferred Doverphos S-9228 leads to improved LTHS properties of the polymer.

Figure 2 reflects the corresponding results for samples comprising another phenolic-type antioxidant, i.e. 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione (Cyanox 1790 <sup>TM</sup>, AO-I-2).

These results show that, by doubling the concentration of Cyanox 1790 <sup>TM</sup> (AO-I-2) from 300 ppm to 600 ppm, only a slight increase in LTHS was achieved for both Irgafos 168 <sup>TM</sup> (AO-II-1) and Doverphos S-9228 <sup>TM</sup> (AO-II-2), but by replacing 1600 ppm Irgafos 168 <sup>TM</sup> (AO-II-1) with 800 ppm Doverphos S-9228 <sup>TM</sup> (AO-II-2), the LTHS increased by more than 700 hours (1 month) at 150°C. This finding is surprising in view of the prior art and shows a synergistic effect for the compounds as used.

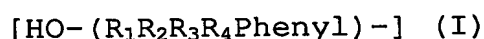
2000 ppm of the talc Tital 10 <sup>TM</sup> (Incemin, Inc.) seems to have only a minor or no effect on both process stability and LTHA (Table 2). In this respect, it is to be noted that Tital 10 <sup>TM</sup> is a very pure talc.

Claims

1. A stabilized polymer composition comprising a polymer  
and an antioxidant composition for improving the long term  
5 heat stability of polymers, in particular polyolefins, said  
antioxidant composition comprising:

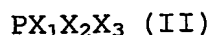
(a) 0,01% - 0,5% by weight of at least one sterically  
hindered phenolic compound, wherein said phenolic compound  
contains at least one phenolic moiety of general formula (I):

10



wherein  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  or  $\text{R}_4$  may be the same or different and at  
least one of  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  or  $\text{R}_4$  is selected from the group  
15 consisting of branched alkyl having 1 to 12 carbon atoms,  
preferably tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl  
and adamantyl, the others of  $\text{R}_1$ ,  $\text{R}_2$ ,  $\text{R}_3$  or  $\text{R}_4$  being H or lower  
alkyl having 1 to 6 carbon atoms;

20 (b) 0,01% - 0,5% by weight of at least one phosphorous  
compound, wherein said phosphorous compound contains at least  
one phosphorous compound moiety of general formula (II):



25

wherein  $\text{X}_1$  may be  $\text{R}_5$  or  $\text{OR}_5$ ,  $\text{X}_2$  may be  $\text{R}_6$  or  $\text{OR}_6$ ,  $\text{X}_3$  may be  $\text{R}_7$   
or  $\text{OR}_7$  and  $\text{R}_5$ ,  $\text{R}_6$  or  $\text{R}_7$  may be the same or different and at  
least one of  $\text{R}_5$ ,  $\text{R}_6$  or  $\text{R}_7$  is selected from the group  
consisting of  $\text{C}_1$ - $\text{C}_{25}$  alkyl group, aryl group or aralkyl group  
30 which may be substituted by lower alkyl having 1 to 6 carbon  
atoms, or two or any of  $\text{R}_5$ ,  $\text{R}_6$  or  $\text{R}_7$  may form a ring structure  
having 4 to 12 carbon atoms,



(c) 0,01% - 1% by weight of at least one sulphur-containing compound of general formula (III):



5

wherein  $x = 1$  or  $2$ , and wherein  $R_8$  and  $R_9$  may be the same or different and are selected from the group consisting of  $C_{10}$ - $C_{25}$  alkyl groups optionally being substituted with  $C_1$ - $C_{12}$  alkyl ester carboxylates,

10 wherein said % by weight values are referred to the polymer composition.

2. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, 15 wherein said antioxidant composition comprises:

(a) 0,02% - 0,2% by weight of said at least one sterically hindered phenolic compound,

(b) 0,03% - 0,2% by weight of said at least one phosphorous compound, and

20 (c) 0,05% - 0,6% by weight of said at least one sulphur-containing compound of general formula (III), wherein said % by weight values are referred to the polymer composition.

25 3. A stabilized polymer composition according to claim 1, comprising a polyolefin and an antioxidant composition, wherein said antioxidant composition comprises:

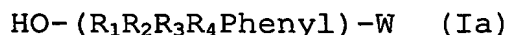
(a) 0,03% - 0,15% by weight of said at least one sterically hindered phenolic compound,

30 (b) 0,05% - 0,15% by weight of said at least one phosphorous compound, and

(c) 0,1% - 0,5% by weight of said at least one sulphur-containing compound of general formula (III),

wherein said % by weight values are referred to the polymer composition.

4. The stabilized polymer composition of any of claims 1 to 3, wherein the phenolic compound contains at least one phenolic moiety of general formula (Ia):



10 wherein  $\text{R}_1$  and  $\text{R}_4$  being in the 2- and 6-position of the phenol residue may be the same or different and are selected from the group consisting of preferably branched  $\text{C}_1$  to  $\text{C}_{12}$  alkyl, particularly tert.-butyl, iso-propyl, cyclohexyl, cyclopentyl and adamantyl residues,  $\text{R}_2$  and  $\text{R}_3$  having the meaning as given  
15 before, and  $\text{W}$  is selected from  $\text{C}_1$  to  $\text{C}_{12}$  alkyl,  $\text{C}_1$  to  $\text{C}_{12}$  alkoxy,  $\text{C}_1$  to  $\text{C}_{12}$  alkyl carboxylate or  $\text{C}_1$  to  $\text{C}_{12}$  alkyl substituted by another group of the formula  $\text{HO}-(\text{R}_1\text{R}_2\text{R}_3\text{R}_4\text{Phenyl})-$ , wherein  $\text{R}_1$  to  $\text{R}_4$  have the meaning as indicated before.

20 5. The stabilized polymer composition of any of claims 1 to 4, wherein the phosphorous compound comprises a phosphite moiety of the formula  $\text{Bis}(\text{R}_{10})$ -pentaerythrityldiphosphite, wherein  $\text{R}_{10}$  is selected from  $\text{C}_1$ - $\text{C}_{25}$  alkyl group or aryl group  
25 which may be substituted by lower alkyl having 1 to 6 carbon atoms.

6. The stabilized polymer composition of any of claims 1 to 5, wherein the sulphur-containing compound of general  
30 formula (III):



is selected from Di(C<sub>1</sub>-C<sub>20</sub>)alkyl-(S)<sub>x</sub>-di-carboxylate wherein the carboxylic acid is selected from C<sub>1</sub> to C<sub>12</sub> alkyl carboxylic acids.

- 5           7. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:
- 2,6-Di-tert.-butyl-4-methyl phenol;
  - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-
  - 10 hydroxyphenyl)-propionate;
  - Octadecyl 3-(3',5'-di-tert.-butyl-4-
  - hydroxyphenyl)propionate;
  - 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-
  - hydroxyphenyl) benzene;
  - 15       - 2,2'-Thiodiethylene-bis-(3,5-di-tert.-butyl-4-
  - hydroxyphenyl)-propionate;
  - Calcium-(3,5-di-tert.-butyl-4-hydroxy benzyl monoethyl-
  - phosphonate);
  - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-
  - 20 isocyanurate;
  - Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl) butanoic
  - acid)-glycolester;
  - 4,4'-Thiobis (2-tert.-butyl-5-methylphenol);
  - 2,2'-Methylene-bis(6-(1-methyl-cyclohexyl)para-cresol);
  - 25       - N,N'-hexamethylene bis(3,5-di-tert. Butyl-4-hydroxy-
  - hydrocinnamamide;
  - 2,5,7,8-Tetramethyl-2(4',8',12'-trimethyltridecyl)
  - chroman-6-ol;
  - 2,2'-Ethylidenebis(4,6-di-tert.-butylphenol);
  - 30       - 1,1,3-Tris(2-methyl-4-hydroxy-5-tert.-
  - butylphenyl)butane;
  - 1,3,5-Tris(4-tert.-butyl-3-hydroxy-2,6-dimethylbenzyl)-
  - 1,3,5-triazine-2,4,6-(1H,3H,5H)-trione;

- 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane;
- 1,6-Hexanediyl-bis(3,5-bis(1,1-dimethylethyl)-4-hydroxybenzene-propanoate);
- 2,6-Di-tert.-butyl-4-nonylphenol;
- 3,5-Di-tert.-butyl-4-hydroxyhydrocinnamic acid triester with 1,3,5-tris(2-hydroxyethyl)-s-triazine-2,4,6(1H,3H,5H)-trione;
- 4,4'-Butylidenebis(6-tert. Butyl-3-methylphenol);
- 2,2'-Methylene bis(4-methyl-6-tert.-butylphenol);
- 2,2-Bis(4-(2-(3,5-di-t-butyl-4-hydroxyhydrocinnamoyloxy))ethoxyphenyl))propane;
- Triethyleneglycol-bis-(3-tert.-butyl-4-hydroxy-5-methylphenyl) propionate;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C<sub>13</sub>-C<sub>15</sub>-branched and linear alkyl esters;
- 6,6'-Di-tert.-butyl-2,2'-thiodi-p-cresol;
- Diethyl((3,5-bis(1,1-dimethylethyl)-4-hydroxyphenyl)methyl) phosphonate;
- 4,6-Bis(octylthiomethyl)o-cresol;
- Benzenepropanoic acid, 3,5-bis(1,1-dimethylethyl)-4-hydroxy-, C<sub>7</sub>-C<sub>9</sub>-branched and linear alkyl esters;
- 1,1,3-Tris[2-methyl-4-[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionyloxy]-5-t-butylphenyl] butane; and
- Butylated reaction product of p-cresol and dicyclopentadiene.

8. The stabilized polymer composition of any of the precedent claims, wherein the phosphorous compound is selected from the group consisting of:

- Tris(2,4-di-t-butylphenyl) phosphite;

- Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite
  - Bis (2,4-di-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 5     - Di-stearyl-pentaerythrityl-di-phosphite;
- Tris-nonylphenyl phosphite;
- Bis(2,6-di-t-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
- 2,2'-Methylenebis (4,6-di-t-butylphenyl) octyl-
- 10    phosphite;
- 1,1,3-Tris (2-methyl-4-ditridecyl phosphite-5-t-butylphenyl) butane;
- 4,4'-Butylidenebis (3-methyl-6-t-butylphenyl-di-tridecyl) phosphite;
- 15    - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite;
- Bis(2-methyl-4,6-bis(1,1-dimethylethyl)phenyl)phosphorous acid ethylester;
- 2,2',2''-Nitrilo triethyl-tris(3,3',5,5'-tetra-t-butyl-1,1'-biphenyl-2,2'-diyl)phosphite);
- 20    - - Phosphorous acid, cyclic butylethyl propandiol, 2,4,6-tri-t-butylphenyl ester; Bis (2,4,6-tri-t-butylphenyl)-pentaerythrityl-di-phosphite;
- 2,2'-Ethylidenebis (4,6-di-t-butylphenyl) fluorophosphonite
- 25    - 6- (3-tert-Butyl-4-hydroxy-5-methylphenyl) propoxy)-2,4,8,10-tetra-tert. butyldibenz (d,t) (1.3.2) dioxaphosphopin; and
- Tetrakis-(2,4-di-t-butyl-5-methyl-phenyl)-4,4'-biphenylen-di-phosphonite.

30

9. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is selected from the group consisting of:

- Di-stearyl-thio-di-propionate;
- Di-palmityl/stearyl-thio-di-propionate;
- Di-lauryl-thio-di-propionate;
- Di-tridecyl-thio-di-propionate;
- 5 - Di-myristyl-thio-di-propionate;
- Pentaerythritol octyl thiodipropionate;
- Lauryl-stearyl-thio-di-propionate;
- Di-octadecyl-disulphide;
- Di-tert-dodecyl-disulphide and
- 10 - Pentaerythritol-tetrakis-(3-laurylthiopropionate)

10. The stabilized polymer composition of any of the preceding claims, wherein the sterically hindered phenolic compound is selected from the group consisting of:

- 15 - Pentaerythrityl-tetrakis(3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)-propionate;
- Octadecyl 3-(3',5'-di-tert.-butyl-4-hydroxyphenyl)propionate;
- 1,3,5-Trimethyl-2,4,6-tris-(3,5-di-tert.-butyl-4-hydroxyphenyl) benzene;
- 20 - 1,3,5-Tris(3',5'-di-tert.-butyl-4'-hydroxybenzyl)-isocyanurate;
- Bis-(3,3-bis-(4'-hydroxy-3'-tert.-butylphenyl)butanoic acid)-glycolester; and
- 25 - 3,9-Bis(1,1-dimethyl-2-(beta-(3-tert.-butyl-4-hydroxy-5-methylphenyl)propionyloxy)ethyl)-2,4,8,10-tetraoxaspiro(5,5)undecane.

11. The stabilized polymer composition of any of the preceding claims, wherein the phosphite compound is selected from the group consisting of:

- 30 - Tetrakis-(2,4-di-t-butylphenyl)-4,4'-biphenylen-di-phosphonite;

- Bis(2,6-di-*t*-butyl-4-methylphenyl)pentaerythrityl-di-phosphite;
  - Di-stearyl-pentaerythrityl-di-phosphite; and
  - Bis(2,4-dicumylphenyl)pentaerythritol diphosphite.

5

12. The stabilized polymer composition of any of the preceding claims, wherein the sulphur-containing compound is Di-stearyl-thio-di-propionate or Di-*tert*-dodecyl-disulphide.

10 13. The stabilized polymer composition of any of any of the preceding claims, wherein

(a) the sterically hindered phenolic compound is 1,3,5-Tris(4-*tert*.-butyl-3-hydroxy-2,6-dimethylbenzyl)-1,3,5-triazine-2,4,6-(1H,3H,5H)-trione or pentaerythrityl-tetrakis(3-(3',5'-di-*tert*.-butyl-4-hydroxyphenyl)-propionate;

15 (b) the phosphite compound is bis(2,4-dicumylphenyl)pentaerythritol diphosphite; and

(c) the sulphur-containing compound is Di-stearyl-thio-di-propionate.

20

14. The stabilized polymer composition of any of claims 1-13, wherein said composition further comprises metal deactivators and/or UV-stabilisers.

25 15. The stabilized polymer composition of claim 14, wherein said UV-stabilizers are sterically hindered amines.

16. The stabilized polymer composition of any of claims 1-16 wherein said polymer is selected from the group consisting of polyolefins, polyethers, polyimides, polyamides and polyesters or mixtures thereof.

30

17. The stabilized polymer composition of claim 16, wherein said at least one polymer is a homo- or co-polymer of polyethylene, polypropylene and polybutadiene.

5 18. Use of the antioxidant composition as defined in any of claims 1-14 for reducing degradation of a polymeric material during processing and end use of said polymeric material.

10 19. The use of claim 18 for increasing long term thermal stability of the polymeric material.

20. Method for producing a polymeric article having an improved long term thermal stability against ageing by radical degradation processes comprising the steps of:

15 (a) providing an unstabilised base polymer material;

(b) adding to said base polymer material the antioxidant composition as defined in any of the preceding claims;

(c) converting the composition obtained in step (b) in a

20 melt-forming process; and

(d) confectioning the polymeric material obtained in step (c).

21. The method of claim 19 further comprising adding

25 other stabilisers and/or modifiers before the converting step c).

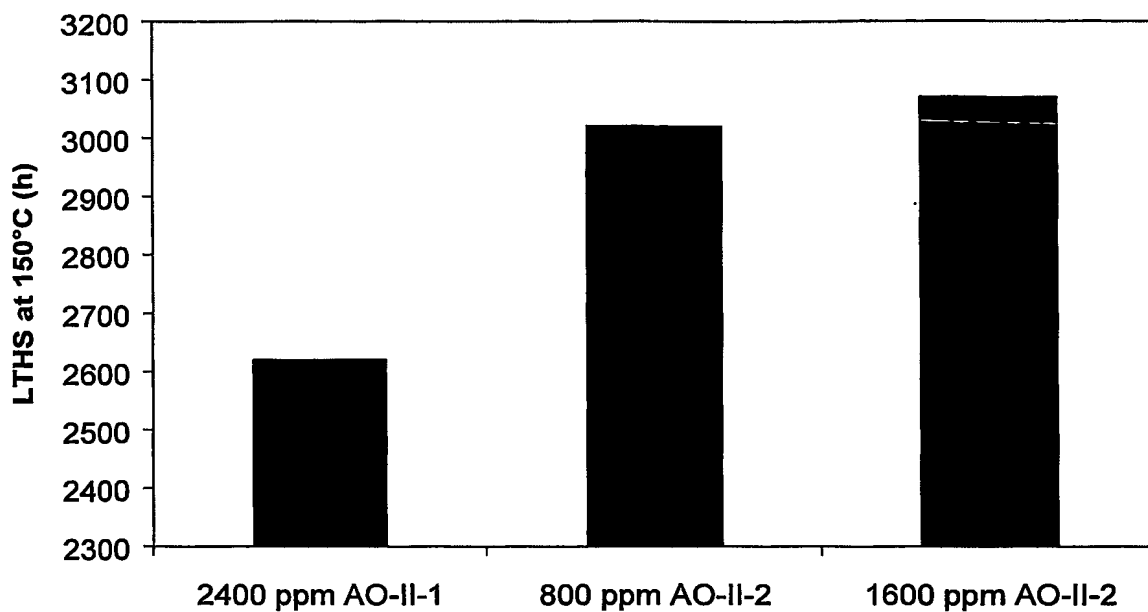
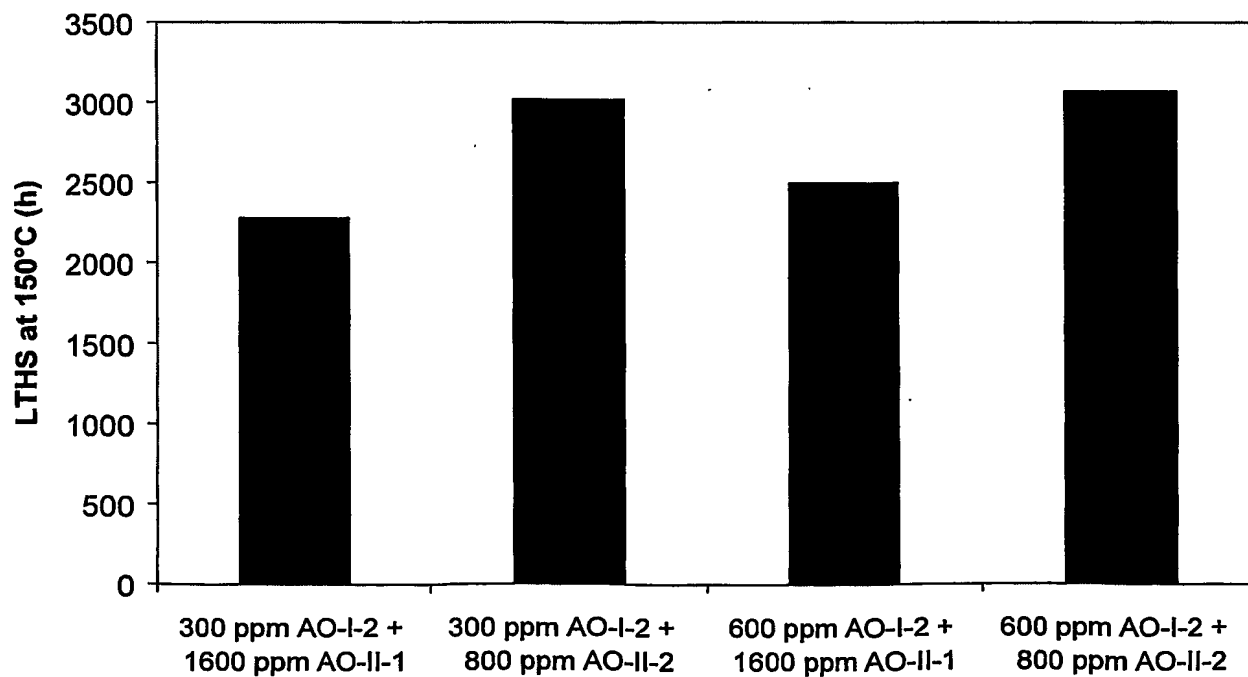
22. The method of any of claims 20 or 21, wherein the converting step includes injection moulding, blow moulding,

30 rotational moulding and extrusion.

23. The method of any of claims 20 to 22, wherein the confectioning step includes cutting, lamination and/or welding.



24. Polymeric article having an increased long term ageing stability obtained by the method of any of claims 20-23.

Figure 1Figure 2

## INTERNATIONAL SEARCH REPORT

International Patent No.

PCT/EP 02/11258

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C08K5/00 //(C08K5/00, 5:13, 5:527, 5:372)

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 200138 Derwent Publications Ltd., London, GB; Class A17, AN 2001-365817 XP002243985 & RU 2 166 217 C (REAL SERVICE CABLE CORP) , 27 April 2001 (2001-04-27) abstract	1-4, 6-10, 12, 14, 16, 18
X	EP 0 330 256 A (ENICHEM SINTESI) 30 August 1989 (1989-08-30) examples claims 1, 4, 5, 8, 9	1-10, 14-18
X	US 6 274 678 B1 (SHINOZAKI TETSUNORI ET AL) 14 August 2001 (2001-08-14)  table 3	1-3, 5-9, 11-16, 18, 19

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

11 June 2003

Date of mailing of the international search report

24/06/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
 NL - 2280 HV Rijswijk  
 Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
 Fax: (+31-70) 340-3016

Authorized officer

Rose, E

## INTERNATIONAL SEARCH REPORT

International Publication No.

PCT/EP 02/11258

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 827 979 A (IDEMITSU KOSAN CO) 11 March 1998 (1998-03-11) claims 1,5,19 ---	1-3,5-9, 14,18
X	EP 0 450 304 A (MITSUI PETROCHEMICAL IND) 9 October 1991 (1991-10-09)  claims 6,8 ---	1-3,5-9, 12,14, 16,18
X	US 5 298 540 A (PAUQUET JEAN-ROCH ET AL) 29 March 1994 (1994-03-29)  claims 1,6,10 ---	1-3,5-9, 12,14, 18,19
X	EP 0 423 346 A (MITSUI PETROCHEMICAL IND) 24 April 1991 (1991-04-24)  claim 5 ---	1-3,5-9, 12,14, 16,18,19
X	EP 0 343 863 A (MITSUI PETROCHEMICAL IND) 29 November 1989 (1989-11-29) claims 1,2,8 ---	1-10,12, 14,16-19
X	EP 0 227 948 A (BORG WARNER CHEMICALS INC) 8 July 1987 (1987-07-08)  claims 1-17 ---	1-3,5,6, 8,9,12, 14,16-18
X	EP 0 115 885 A (STAMICARBON) 15 August 1984 (1984-08-15) claims 1-9 -----	1-10,12, 14,18

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/11258

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
RU 2166217 C	27-04-2001	RU 2166217 C1	27-04-2001
EP 0330256 A	30-08-1989	IT 1215943 B	22-02-1990
		AT 184299 T	15-09-1999
		AU 3015989 A	24-08-1989
		BR 8900908 A	24-10-1989
		CA 1330483 A1	05-07-1994
		DE 68929067 D1	14-10-1999
		DE 68929067 T2	24-02-2000
		EP 0330256 A2	30-08-1989
		JP 1282228 A	14-11-1989
		JP 7119318 B	20-12-1995
		KR 9202870 B1	06-04-1992
		MX 169560 B	12-07-1993
		RU 2054017 C1	10-02-1996
		US 5155153 A	13-10-1992
		ZA 8901114 A	29-11-1989
US 6274678 B1	14-08-2001	US 2002006993 A1	17-01-2002
		US 6284857 B1	04-09-2001
		US 2002032296 A1	14-03-2002
EP 0827979 A	11-03-1998	JP 8302117 A	19-11-1996
		DE 69619669 D1	11-04-2002
		DE 69619669 T2	29-08-2002
		EP 0827979 A1	11-03-1998
		US 6214909 B1	10-04-2001
		WO 9635752 A1	14-11-1996
EP 0450304 A	09-10-1991	AT 137512 T	15-05-1996
		AT 161554 T	15-01-1998
		CA 2037002 A1	28-08-1991
		CN 1054425 A ,B	11-09-1991
		CN 1064689 A ,B	23-09-1992
		CN 1064690 A ,B	23-09-1992
		CN 1064489 A ,B	16-09-1992
		CS 9100490 A2	15-10-1991
		DE 69119132 D1	05-06-1996
		DE 69119132 T2	02-10-1996
		DE 69128546 D1	05-02-1998
		DE 69128546 T2	14-05-1998
		DK 450304 T3	17-06-1996
		DK 630916 T3	04-05-1998
		EP 0450304 A2	09-10-1991
		EP 0630916 A2	28-12-1994
		ES 2088784 T3	16-09-1996
		ES 2111815 T3	16-03-1998
		GR 3019812 T3	31-08-1996
		GR 3026040 T3	30-04-1998
		HK 216296 A	27-12-1996
		JP 3296512 A	27-12-1991
		KR 9403955 B1	09-05-1994
		PL 289219 A1	24-08-1992
		RO 107954 B1	31-01-1994
		SG 42919 A1	17-10-1997
		SG 65030 A1	25-05-1999
		RU 2091401 C1	27-09-1997
		US 5290896 A	01-03-1994

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/11258

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0450304	A	JP 3296510 A AT 138082 T CA 2037025 A1 CS 9100491 A2 DE 69119447 D1 DE 69119447 T2 EP 0444606 A1 HK 216196 A JP 4249557 A KR 9309263 B1 PL 289217 A1 PL 168645 B1 PL 167983 B1 RO 107953 B1 SG 43726 A1 RU 2095375 C1 US 5324805 A JP 4249558 A JP 4249559 A JP 4249560 A CN 1055368 A , B	27-12-1991 15-06-1996 28-08-1991 15-10-1991 20-06-1996 17-10-1996 04-09-1991 27-12-1996 04-09-1992 25-09-1993 24-08-1992 29-03-1996 30-12-1995 31-01-1994 14-11-1997 10-11-1997 28-06-1994 04-09-1992 04-09-1992 04-09-1992 16-10-1991
US 5298540	A 29-03-1994	CA 2063970 A1 DE 59209680 D1 EP 0506614 A2 ES 2132114 T3 JP 3248002 B2 JP 5132577 A	28-09-1992 02-06-1999 30-09-1992 16-08-1999 21-01-2002 28-05-1993
EP 0423346	A 24-04-1991	AT 192471 T CA 2025021 A1 DE 69033537 D1 DE 69033537 T2 EP 0423346 A1 EP 0652253 A2 ES 2147582 T3 WO 9008173 A1 JP 2851942 B2 KR 9200170 B1 US 5395869 A	15-05-2000 13-07-1990 08-06-2000 11-01-2001 24-04-1991 10-05-1995 16-09-2000 26-07-1990 27-01-1999 09-01-1992 07-03-1995
EP 0343863	A 29-11-1989	AT 109815 T CA 1334459 A1 CN 1039432 A DE 68917374 D1 DE 68917374 T2 EP 0343863 A2 JP 2049044 A KR 9108782 B1 JP 2043235 A JP 2043237 A JP 2077456 A JP 2043239 A JP 2043240 A JP 2049045 A JP 2043241 A	15-08-1994 14-02-1995 07-02-1990 15-09-1994 01-12-1994 29-11-1989 19-02-1990 21-10-1991 13-02-1990 13-02-1990 16-03-1990 13-02-1990 13-02-1990 19-02-1990 13-02-1990
EP 0227948	A 08-07-1987	DE 3688241 D1	13-05-1993

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/11258

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0227948	A	DE 3688241 T2	16-09-1993
		EP 0227948 A2	08-07-1987
		JP 7107112 B	15-11-1995
		JP 62174244 A	31-07-1987
		KR 9502555 B1	21-03-1995
EP 0115885	A	NL 8300064 A	01-08-1984
	15-08-1984	EP 0115885 A1	15-08-1984